



## Short communication

## A divalent quaternary alkyl ammonium salt as the electrolyte for high-energy electric double-layer capacitors

Cheng Zheng<sup>a,b,1</sup>, Masaki Yoshio<sup>c</sup>, Li Qi<sup>a,1</sup>, Hongyu Wang<sup>a,\*</sup><sup>a</sup> State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, China<sup>b</sup> Graduate University of Chinese Academy of Sciences, Beijing 100039, China<sup>c</sup> Advanced Research Center, Saga University, 1341 Yogo-machi, Saga 840-0047, Japan

## H I G H L I G H T S

- Divalent salt based on tetramethyl piperazine as the electrolyte.
- Divalent cations enlarge capacities of electric double-layer capacitors (EDLCs).
- Heavy solvation of divalent cations has negative effects.
- The electrolyte solutions have low ionic conductivity.
- EDLCs using the divalent salt show poor cycle performance.

## A R T I C L E I N F O

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## A B S T R A C T

A divalent electrolyte salt based on 1,1,4,4-tetramethyl piperazine has been synthesized and applied in electric double-layer capacitors (EDLCs). Traits of the divalent salts have been accessed as well as monovalent quaternary alkyl ammonium salts by the means of galvanostatic charge–discharge tests and ionic conductivity measurements. Compared with monovalent salts, the divalent salts do enlarge the charge storage ability of EDLCs remarkably. However, highly concentrated charge density on the divalent cation has a strong interaction with the organic solvent of propylene carbonate. The adverse effect of this heavy solvation on the performance of EDLCs has been investigated. Moreover, the influence of pore size distribution on the storage ability of these cations at the porous carbon electrode has been addressed.

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## 1. Introduction

Nowadays, electrochemical capacitors have drawn much attention as a kind of unique electric energy storage devices. Their present market is still dominated by the tradition electric double-layer capacitors (EDLCs) composed of two symmetrical porous carbon electrodes [1,2]. In order to expand their application fields, an urgent task should be fulfilled right now. That is to elevate their energy densities with little sacrifice of power densities [3]. One prerequisite for this target is to widen their working voltage ranges by using non-aqueous electrolyte solutions, in which monovalent quaternary alkyl ammonium salts of strong acids are dissolved

[4–6]. In fact, all the quaternary alkyl ammonium cations have bigger ionic radii than the popular anions such as  $\text{BF}_4^-$ ,  $\text{ClO}_4^-$  and  $\text{PF}_6^-$ . Therefore, given the same space to accommodate ions, the storage amounts of quaternary alkyl ammonium cations must be smaller than those corresponding to the tiny anions. So the low specific capacitance values of porous carbon negative electrodes (corresponding to the adsorption of monovalent quaternary alkyl ammonium cations) become the bottleneck of charge storage in EDLCs.

Recently, it has been realized that “doubly charged” ammonium salts based on diazabicyclo[2,2,2]octanediium moiety (for example, the left cation as shown in Fig. 1) may contribute to comparatively high energy densities of EDLCs [7,8]. These cations have the  $D_{3h}$  symmetry. In contrast, we design another divalent quaternary alkyl ammonium salt with  $D_{2h}$  symmetry (the right cation in Fig. 1). Tetramethyl ammonium ( $\text{TMA}^+$ ) is considered as the smallest quaternary alkyl ammonium. If two tetramethyl ammonium units are

\* Corresponding author. Tel./fax: +86 431 85262287.

E-mail addresses: [hongyuwang@ciac.jl.cn](mailto:hongyuwang@ciac.jl.cn), [wanghongyu@hotmail.com](mailto:wanghongyu@hotmail.com) (H. Wang).<sup>1</sup> Tel./fax: +86 431 85262287.

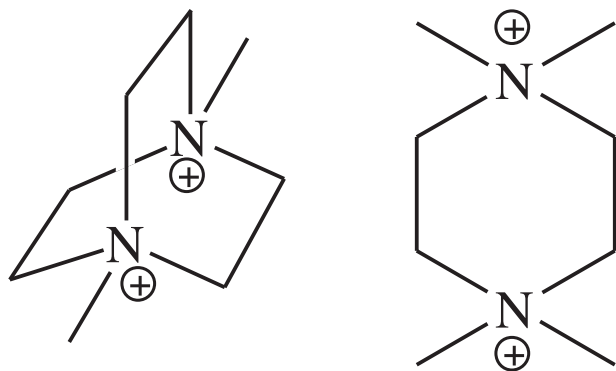


Fig. 1. Chemical structures of divalent quaternary alkyl ammonium cations (the left DMDABCO<sup>++</sup> in Ref. [7] and the right TMP<sup>++</sup> in this study).

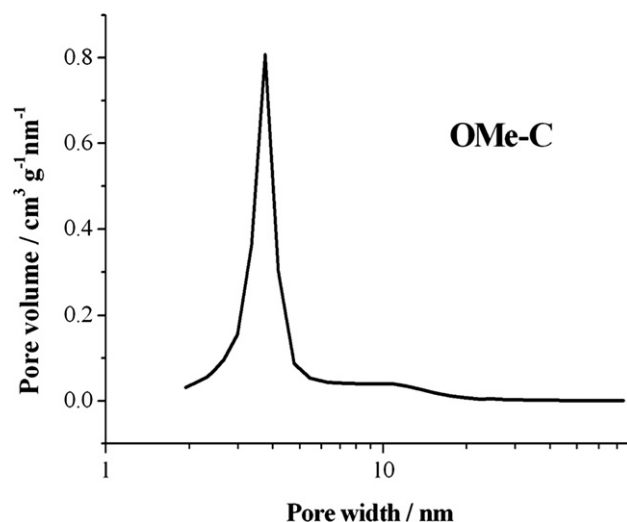


Fig. 2. Pore size distribution of OMe-C.

stacked together, and bridged through two adjacent methyl groups, one divalent quaternary alkyl ammonium (1,1,4,4-tetramethyl piperazine, TMP<sup>++</sup>) can be got. Each cation in this salt carries two charges. If the same amount of cations were accommodated in the pores of carbon negative electrode, divalent cations might contribute to near twice the specific capacitance value originated from the adsorption of monovalent ammonium cations. On the other hand, in spite of the close formula weights of TMP<sup>++</sup> (FW = 144) and *N,N*-1,4-diazabicyclo[2,2,2]octanediium (DMDABCO<sup>++</sup>, FW = 142), the solubility of TMP(BF<sub>4</sub>)<sub>2</sub> (~1.2 M) is much higher than that of DMDABCO(BF<sub>4</sub>)<sub>2</sub> (~0.3 M) in the solvent of propylene carbonate (PC), which fact can also be empirically judged by the asymmetry degree of molecular formula. High solubility of salts in the electrolyte solutions plays a very important role in satisfactory EDLCs [9,10]. In this sense, the new salt (TMP(BF<sub>4</sub>)<sub>2</sub>) in this study is more advantageous. However, due to the concentrated charge density in TMP<sup>++</sup> cation, it has a strong attraction towards the surrounding organic solvent molecules and then forms a tight solvation sheath in the electrolyte solutions. This fact may exert a very complex influence on the performance of porous carbon negative electrodes. At first, the solvation sheath can enlarge the occupation volume of each cation and then decrease the accumulation numbers in the pores of carbon electrodes [11]. Second, the solvent sheath is liable to cathodic decompositions during the charge process of an EDLC. Third, although some desolvation of cations in subnanometer pores may lead to the “anomalous increase in capacitance” of porous carbon negative electrodes, it may cost some extra activation energy and retard the rate capability of EDLCs. The above considerations inspired our interest on the compatibility between the divalent ammonium cation and the pore structure of carbon electrodes. In this study, the electrochemical performance of EDLCs using the nonaqueous electrolytes based on the divalent as well as the monovalent quaternary alkyl ammoniums has been investigated.

## 2. Experimental

Electrode materials included the microporous carbon (Mi-C) (PW15M13130 from Kureha Co. Ltd.) and the ordered mesoporous carbon (OMe-C) made in our lab. Some physical properties of the Mi-C material have been described in the past reports [12,13]. The preparation procedure of OMe-C was in accordance with the previous study [14]. The B.E.T. specific surface area value of OMe-C is 881.8 m<sup>2</sup> g<sup>-1</sup> and the pore size distributes mainly in the range from 3 to 5 nm as shown in Fig. 2. In an EDLC (coin cell), the weight ratio of negative to positive electrode materials was kept at 1. The electrolytes were quaternary alkyl ammonium salts dissolved in PC solvent. BF<sub>4</sub><sup>-</sup> was picked up as the counter anion in these salts while

PC was used as the solvent, unless otherwise specified. PC was battery grade with the water content of 7.3 ppm. The monovalent quaternary alkyl ammonium cations consisted of tetramethyl ammonium (TMA<sup>+</sup>), ethyltrimethyl ammonium (ETMA<sup>+</sup>), diethyltrimethyl ammonium (DEDMA<sup>+</sup>), triethylmethyl ammonium (TEMA<sup>+</sup>), tetraethyl ammonium (TEA<sup>+</sup>), tetrapropyl ammonium (TPA<sup>+</sup>), tetrabutyl ammonium (TBA<sup>+</sup>), and spiro-(1,1′)-bipyrrolidinium (SBP<sup>+</sup>). The divalent quaternary alkyl ammonium cations comprised of DMDABCO<sup>++</sup> and TMP<sup>++</sup>. These cations were synthesized by the methylation of 1,4-diazabicyclo[2,2,2]octane and piperazine, respectively, according to the Ue–Mori procedure [15]. TMP<sup>++</sup> has been identified by <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ=3.19 (br, 8H), 3.09 (s, 12H). The coin cell fabrication and glove box conditions were similar to those described in the past reports [12,13]. The galvanostatic charge–discharge tests of the coin cells were performed at the constant current density of 0.4 mA cm<sup>-2</sup>. The cut-off voltages were set as 0 and 2.7 V. Charge storage ability of the total capacitor (coin cell) was expressed in the terms of capacity (mA h g<sup>-1</sup>). The capacity values were calculated according to the following formula:  $Q = It/w_+$  ( $I$ , the constant current (mA);  $T$ , the time for charge or discharge between cut-off voltages (h);  $w_+$ , the weight of the positive electrode material (g)).

## 3. Results and discussion

The superiority of divalent to monovalent quaternary alkyl ammonium-related electrolyte salts can be directly assessed from the galvanostatic charge–discharge results. For all the electrolyte salts (either mono- or divalent quaternary alkyl ammonium-based), typical galvanostatic discharge curves of EDLCs demonstrate the linear feature as shown in Fig. 3. From these curves, we obtained the discharge capacities delivered by EDLCs using different electrolyte salts dissolved in PC solvent, as compared in Fig. 4. In the EDLCs using monovalent quaternary alkyl ammonium-based electrolyte salts, the discharge capacity is limited (<36 mA h g<sup>-1</sup>), even though it can be increased to some extents by decreasing the formula weight of quaternary alkyl ammonium. It is generally believed that smaller cations give rise to bigger storage ability of porous carbon negative electrode. However, in an “extreme” case, for the electrolyte salt based on the smallest quaternary alkyl ammonium cation (TMABF<sub>4</sub>), the corresponding discharge capacities of EDLCs don’t provide the maximum values. These relatively low discharge capacity values delivered by EDLCs using TMABF<sub>4</sub> are

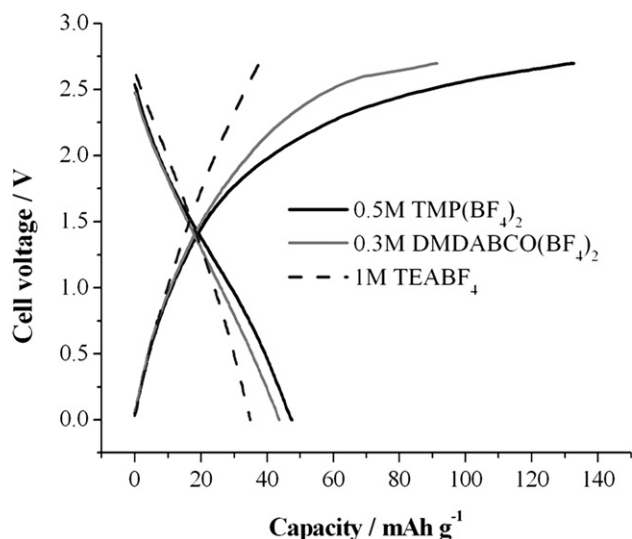


Fig. 3. Initial charge–discharge curves of Mi-C/Mi-C EDLCs using different electrolytes dissolved in PC.

mainly due to the low solubility of TMAF<sub>4</sub> in PC (0.1 M) [4]. In contrast to the above results, the employment of divalent quaternary alkyl ammonium salt does promote the discharge capacity values of EDLCs to higher than 45 mA h g<sup>−1</sup>. On the other hand, the heavy solvation of divalent cations will fatten their individual occupation spaces and it is a hard work to get rid of the closely-bond solvent sheath. So Mi-C negative electrode may be incompatible with divalent quaternary alkyl ammonium cations since considerable parts of the pores with smaller sizes are not accessible for the bulky solvated cations. Alternatively, OMe-C abundant with mesopores may be a tolerant “host” material to accommodate divalent quaternary alkyl ammonium-related cations. It is of interest to compare the discharge capacity values delivered by OMe-C/OMe-C capacitors against a variety of quaternary alkyl ammonium-based electrolytes. In the cases of small monovalent

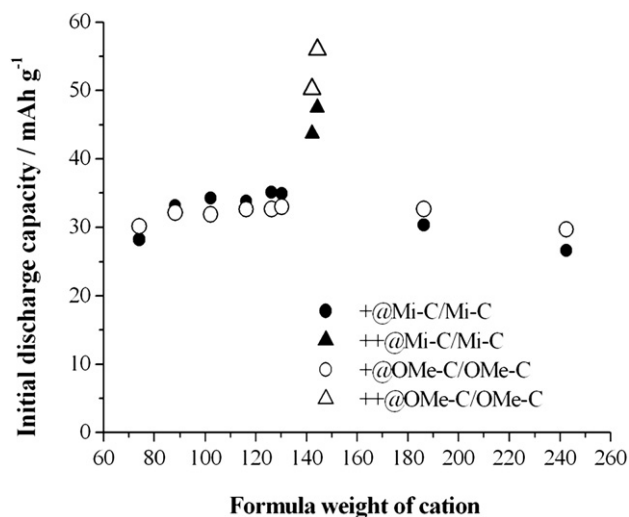


Fig. 4. Relationship between the initial discharge capacity of EDLC and the formula weight of cation (most of the electrolyte salts dissolved in PC have the same concentration of 1 M; the concentrations of TMAF<sub>4</sub>, DMDABCO(BF<sub>4</sub>)<sub>2</sub>, and TMP(BF<sub>4</sub>)<sub>2</sub> in PC are 0.1 M, 0.3 M and 0.5 M, respectively owing to limited salt solubility or viscosity of electrolyte solutions).

cations like ETMA<sup>+</sup>, DEDMA<sup>+</sup>, TEMA<sup>+</sup>, SBP<sup>+</sup>, and TEA<sup>+</sup>, OMe-C/OMe-C capacitors deliver lower discharge capacity values as compared with Mi-C/Mi-C capacitors. On the contrary, for the bigger monovalent cations like TPA<sup>+</sup> and TBA<sup>+</sup>, OMe-C/OMe-C capacitors have higher discharge capacity values than Mi-C/Mi-C capacitors. The above phenomenon implies that OMe-C electrode is more suitable for the adsorption of larger ions. Here the OMe-C/OMe-C capacitor using TMA<sup>+</sup>-based electrolyte seems an exception since its discharge capacity value is somehow higher than that of the Mi-C/Mi-C capacitor. This fact may be an evidence for the considerable solvation of TMA<sup>+</sup> by PC solvent although the solubility of TMAF<sub>4</sub> is very low in PC [16]. Another point worthy of note in Fig. 4 is the significant increase in the discharge capacity delivered by the OMe-C/OMe-C capacitors using the DMDABCO<sup>++</sup> or TMP<sup>++</sup>-based electrolytes, even as high as 55 mA h g<sup>−1</sup>. Then the energy density values of OMe-C/OMe-C capacitors can exceed those of Mi-C/Mi-C capacitors by over 52% if divalent instead of monovalent quaternary alkyl ammonium-based electrolytes are applied in EDLCs.

Nevertheless, the shortcomings of the divalent salts must be properly apprehended in the practical applications. The strong solvation by PC solvent can lead to many negative consequences, one of which is reflected in Fig. 5. At low salt concentrations (≤0.2 M), the PC solutions dissolving divalent electrolyte salts possess higher electrolytic conductivity values than those for monovalent salts. This can be explained by the denser charge carried by divalent cations than monovalent ones. However, with the rise in the salt concentration, the electrolytic conductivity values of divalent salt-based electrolyte solutions become smaller than those of monovalent salt-based electrolyte solutions. This phenomenon may partly be ascribed to the slow movement of bulky PC-solvated divalent cations [4]. Actually, the concentrated TMP(BF<sub>4</sub>)<sub>2</sub>-PC solutions become quite viscous, even look like a colourless and transparent gel. The above fact implies that divalent quaternary alkyl ammonium-based salts are not beneficial for the rate performance (power density) of EDLCs.

Another demerit of the thick solvent sheath around divalent cations is its cathodic decomposition during charge–discharge processes of EDLCs. This severe problem may not only lead to the remarkable irreversible capacity and the reversible capacity fading as illustrated in Fig. 6, but also trigger the gas production as evidenced by the bulge of the coin cells after long charge–discharge

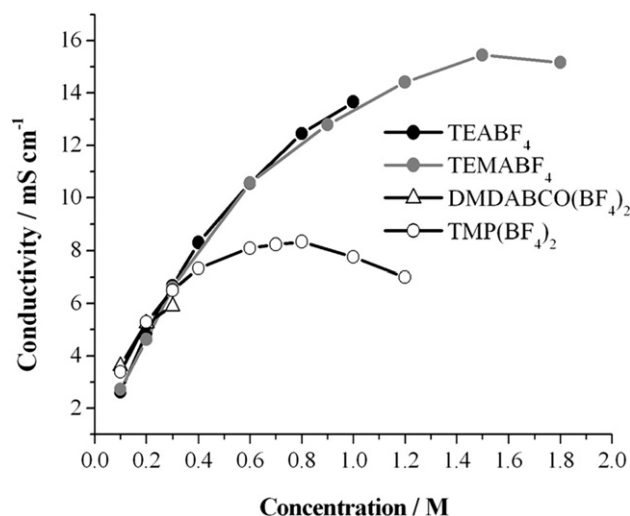


Fig. 5. Relationship between the electrolytic conductivity of PC solution and the concentration of electrolyte salt.

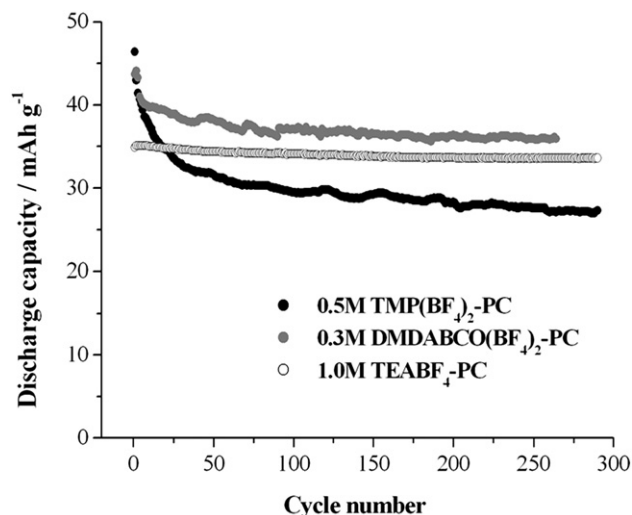


Fig. 6. Cycle performance of Mi-C/Mi-C EDLCs using different electrolyte solutions.

cycles. This is in contrast with the cases of monovalent quaternary alkyl ammonium cations mildly solvated.

#### 4. Conclusion

So far, we have shown that the electrolyte salt of  $\text{TMP}(\text{BF}_4)_2$  does increase the energy density of EDLC significantly. Nevertheless, because of the highly condensed charge density in the cation, the strong attraction between the cation and surrounding solvent molecules may have some negative effects on the electrochemical performance of EDLCs. For example, the co-adsorption of extra

solvent molecules into the pores of carbon negative electrodes is likely to occur, which may lead to the cathodic decomposition of the solvent at the porous carbon negative electrode during charge process. In addition, the sticky solvent sheath around the cation slows down its movement in the electrolyte solutions and decreases the rate capability of EDLCs.

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